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Computing Device Applications of Group IV Nanoparticle Spectroscopy

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Final Report

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Overview

This project intended to study the spectroscopy of colloidal silicon nanoparticles. The investigation assumed various aspects: nanoparticle fabrication; nanoparticle filtration; sample preparation and characterization techniques; laser maintenance; spectroscopy; and theory. Because the available dye laser could not be stabilized for scanning, the anticipated spectroscopy was never performed. Techniques pursued and lessons learned are described.

Nanoparticle Fabrication and Characterization

Low resistivity (~10 - 20 ohm-cm) silicon wafers were electrochemically etched in a 1:3:1 mixture of HF:Methanol:Hydrogen Peroxide, with the silicon wafer serving as the anode and using a platinum wire cathode. Evidently the chemical process consists of oxidation of the silicon by the peroxide followed by etching of the silicon oxide by the hydrofluoric acid. Methanol serves as a buffer. This process results in the formation of a deeply crevassed porous silicon surface. The resulting nodules are reportedly passivated by hydrogen atoms on all dangling silicon bonds, thus prolonging ensuing oxidation. These nodules vary in size from about 1 nm to several hundred nanometers diameter. The larger nodules support smaller ones on their surfaces.

Controlling the etch rate via the electrical current impacts the size of formed nano-nodules. Generally, higher local current densities result in smaller nodules, as evidenced by the visible color variation of subsequent fluorescence under illumination by ultraviolet lamp. Much of the etch process seemingly occurs in the meniscus of the etch bath on the silicon wafer, so controlling the current density accurately – e.g. by the area of submerged wafer – is quantitatively difficult. During the last year of the project, chrome-gold contact strips were deposited on diced sections of wafers to ensure good electrode contact; previously, chrome-plated alligator clips were used directly to contact the wafers, with uncertain contact resistance.

Following etching, the wafers are rinsed in methanol to inhibit further etching by remnant HF, then submerged in fresh methanol in small vials and vibrated ultrasonically, resulting in the release of many of the nodules from the silicon wafer into colloidal suspension. These

suspensions also fluoresce with the same apparent spectra. In suspension, yellow and green fluorescence are even less commonly observed.

There is some evidence that the colloidal particles are not predominantly single nanoparticles, but rather larger aggregates or small nano-nodules on the surfaces of larger particles, as large as several hundred nanometers cross-section. These structures were observed using scanning electron microscopy. Note that the SEM available for our inspection exhibited resolution only down to about 50 nm.

In principle, following particle-in-a-box quantum mechanics applied to silicon excitons, smaller nodules emit shorter wavelength fluorescence. Perhaps surprisingly, only certain relatively narrow bands of fluorescent wavelengths appear. Predominant in our experiments was orange fluorescence, around 630 nm. Yellow and green fluorescence wavelengths were occasionally observed. The literature suggests that blue and red should also appear; red was observed very rarely, and blue (corresponding to the smallest nodules) never. The conceptual foundations for this observation are described in a portfolio of papers by M. Nayfeh. In his model, the smallest nodule comprises 29 silicon atoms, surface passivated by a dozen hydrogens. The central atom is surrounded by tetrahedrally coordinated silicons, forming a 5-atom core. The next shell of 24 silicon atoms is symmetrically arranged in a near-fullerene structure, and forms a quasi-sphere about 1 nm in diameter. This structure should fluoresce in the blue. A second shell of silicon (preceding the hydrogen passivation) enlarges the structure by adding 94 additional silicon atoms. It fluoresces green. Additional shells lead to yellow, orange, and red fluorescence. The validity of this model is discussed below.

It is briefly noted here that other experimentalists (i.e. Vladimir Lysenko at Ecole Centrale de Lyon in France) produce silicon nanoparticles using much more dramatic etch techniques; essentially shattering wafers under high voltage discharge.

Fabricating colloidal silicon from Czochralski-grown wafers is imperative to produce the concentric-shell structures anticipated here. Silicon molecules assembled from atomic vapors in vacuum assume different molecular structures. Some of these are in fact more energetically stable, according to recent models (see below).

Colloidal silicon nanoparticles do not necessarily comprise the desired nanospheres. Many particles are considerably larger than the modeled progression of layered spherical shells would indicate. Some fluorescent emission seemingly arises from quantum-sized nodules attached to larger particles. Various schemes were investigated in attempts to filter nanospheres by size. First, size-exclusion chromatography (also called gel-permeation chromatography) was enlisted. In this process, a slurry of small plastic beads is compacted into a pipette so that the triangular interstices approximate in cross-section the maximum size of nanoparticles expected to pass. Repeated rinsing then flushes these smaller nanoparticles through the filter, trapping larger particles and aggregates. Unfortunately, minimum diameter filter beads still allowed

passage of nanoparticles greater than 200 micron diameter, and the consequent dilution suppresses the fluorescence signal. A second approach intended to determine charge-to-mass ratio using Matrix Assisted Laser Desorption/Ionization (MALDI) mass spectroscopy. Aided by an organic matrix molecule that temporarily binds the molecule of interest, illumination by laser light ionizes the sample molecules from a substrate which then volatilizes in a region of high electric field in vacuum. The field accelerates the liberated ionized nanoparticles through a pair of rotating vanes to an absorptive target; charge-to-mass ratio determines which particles pass the vanes. This method produced undecipherable signal patterns. Subsequently, finer commercial filters were discovered and implemented: Anodisc filters made from etched and oxidized aluminum foils that serendipitously form hexagonal close-packed pores with ~20 nm channels. Perhaps MALDI would be more effective with these filtered samples; still, the expected diameters of colloidal nanospheres range only up to about 3 nm for which 20 nm filters would be largely ineffective.

Individual colloidal nanospheres do scatter incident laser light, as observed with both 532 nm and 633 nm wavelengths. The scattering from colloids encapsulated in planar-sided glass (Starna) cells was detected by a CCD camera, imaged using a microscope objective. Nanospheres were observed migrating across the field of view. In fact, convection heating of the suspending liquid by the laser illumination dominated the movement of the scattering nanospheres. A third concept to characterize nanosphere charge-to-mass ratio referred to the classical Miliken oil drop experiment. The Starna cell was placed between two oppositely charged plates, in anticipation that the imposed drift would dominate both convection and Brownian motion. No effect of the drift voltage was discerned. Speculating that silicon nanospheres might rarely ionize in methanol, the colloidal sample was placed in an X-ray beam to enhance ionization. The cross-section (~1 – 3 nm diameter) of a nanosphere to an X-ray beam, combined with the equally small absorption length, apparently defeated this procedure. No drift of ionized silicon nanospheres was observed.

A freshly prepared surface of highly-ordered pyrolytic graphite (HOPG) was submerged in a vial of colloidal silicon nanoparticles for several minutes, then removed and allowed to air dry. The surface was then imaged using a scanning tunneling microscope. On one sample, a row of peaks appeared, accompanied by several orthogonal side rows of smaller peaks – reminiscent of a mountain range. Speculation hinted that nanospheres were captured at the dihedrals of the HOPG surface. Attempts to characterize the nanosphere diameters were inconclusive, however. In part, it is difficult to ascertain the effective radius of the scanning tip (an etched Ir/Pt wire), which convolves with the scanned object dimension. False images can also present, based on the likelihood of small HOPG or silicon nanostructures attaching to the scanning tip, so that their periodicity is carried across the scan as part of the instrument response.

Finally, a scheme to ascertain nanoparticle mass from vibrational resonance was pursued. The concept relied on trapping nanospheres in an optical lattice, then oscillating the lattice (by diverting the constituent laser beams, or by modulating the laser frequency) at various

frequencies and amplitudes until the trapping potential failed in comparison to inertial forces. A unique optical interference pattern, in three dimensions, was constructed. Pairs of parallel laser beams, displaced by special-order beamsplitters, were incident parallel to the axis of a concave parabolic reflector. By geometrical construction, all such beams pass through the parabola's focus, where an interference pattern thereby is formed. The periodicity of the interference pattern can be varied by shifting a single fold mirror in the incident beam path. Unfortunately, this scheme met its demise when Gaussian diffractive effects were introduced. In order for all beams to have waists at the common parabolic focus, the locus of input beam waists is also required to lie on a virtual parabolic surface because of the variable curvature of the parabola with beam offset. This detail is too difficult to satisfy experimentally. Coincidentally, trapping nanospheres, essentially nanomolecules, is an unresolved problem; NIST scientists were simultaneously pursuing a similar problem. Whereas larger (~10 micron) diameter spheres can be trapped by refraction, and smaller (atoms) spheres can be trapped by resonant dipole scattering, whether intermediate (molecular) spheres exhibit sufficient dipole scattering to overcome larger inertial momentum is uncertain. In addition, such optical traps require at least modest if not ultra-high vacuum environment, so the entire parabolic interferometer would need to be encapsulated in a vacuum environment. Student enthusiasm waned, and the approach stagnated. A reliable means to segregate nanospheres by particle size was not realized.

Spectroscopy Sample Preparation

To separate electronic response from thermal broadening in spectroscopic studies requires cryogenic environment. An optically accessible cryostat is available. Putting the nanospheres into an amenable sample form is necessary. Although methanol solidifies well above liquid helium temperature (the cryostat can access 4 Kelvin), the container which would hold the methanol and its colloidal silicon nanospheres need be glass (or fused silica) and would probably shatter. A cryogenic temperature potting epoxy was procured to serve as host matrix for the nanospheres. At the ultrasound vibration step of nanosphere preparation, after the porous silicon etch and rinse, the porous surface wafers were submerged in the catalyzing component of the epoxy. Subsequently the resultant colloid was mixed with the epoxy resin component and cured. This diluted the colloid sufficiently that fluorescence visible to the eye disappeared. Whether the process quenched the fluorescence because of the molecular environment or because of attendant oxidation was not determined.

An alternative conception to preparing nanospheres for spectroscopic analysis would have resulted from suspending the nanospheres in an optical lattice. There, the host methanol presumably would have evaporated into the vacuum. Whether the dissociation of the host solute would have occurred without entraining the nanospheres simultaneously into the vacuum pump effluent remains unknown.

Laser Stabilization

This project relied on the Autoscan capability of a Coherent 699-29 dye laser pumped by a 20 watt Coherent Verdi (cw ND:Yttrium Vanadate) running at about 6 watts. In order for the dye laser to scan wavelength continuously under computer control, it must lock stably to a reference cavity over a 20 GHz frequency range – essentially the free spectral range of a thick etalon positioned along the internal optical path of the laser. The laser was re-built several times to adjust mirror separations, correct mirror skew around the optical axis established by the structural invar rod, align the pump laser beam with the dye jet, ensure emission parallel to the bench, and provide resonant injection into the reference cavity. Fresh dye was intermittently provided to retain gain efficiency. Although establishing lasing and optimizing power output (especially during insertion of the internal etalons, which ensure uni-directional beam propagation and suppress lateral modes) became routine, laser stability was never sufficient to lock over the requisite 20 GHz bandwidth that would allow computer controlled autoscanning along with registration of the emission wavelength. Mirror quality degradation is suspect, from repeated cleaning over decades of life. A rotating glass plate in the laser cavity alters the effective cavity length, and in so doing minutely varies the point of incidence of the lasing beam on the cavity mirrors, occasionally encountering scattering features that disrupt frequency fidelity. Replacement mirrors are no longer available, even on the refurbished equipment market.

Theoretical and Analytical Aspects

During the period of this project, publications from authors at Lawrence Livermore National Laboratory examined the molecular structure of silicon 29 (as well as of structures with similar numbers of silicon atoms). In particular, three isomers of the silicon filled-cage structure were identified for 29 constituent atoms. One of these corresponds to the bulk Czochralski symmetry, presumably accessible via the porous silicon etch approach to production of nanoparticles. The analysis does show that silicon nanostructures exhibit special stability around the 29-atom size; but that the Czochralski symmetry is not the most stable.

Presumably, aggregation of silicon nano-molecules of 29 atoms from vapor, as in an atomic beam epitaxy process, would result in a mixture of the isomer structures. This potentially precludes such a process from producing the desired nanospheres in the absence of a sensitive scheme for segregation of the isomers.

The spectroscopy of silicon nanospheres was hypothesized for this program to include new features beyond those anticipated from straightforward particle-in-a-box analysis, even admitting spherical symmetry (hence Bessel basis functions). Particularly, electron (or exciton) wavefunctions that circulate on the surface were envisioned, adopting aspects of surface plasmon

polaritons (SPP). This model is supported by the usual establishment of charge accumulation regions at the surface of silicon samples. This charge accumulation has been observed commonly for oxidized silicon surfaces (the substantiating phenomenon for most MOSFET devices), and also for hydrogen passivated silicon surfaces. For planar silicon, the accumulation layer thickness is perhaps tens of nanometers – greater than the silicon nanosphere diameter. Whether surface curvature and quantum effects reduce this thickness on small particles remains undetermined. (Extant models do admit that excitons on quantum dots often harbor the ‘hole’ component at the center while the electron component orbits, sometimes with its center of distribution outside the nominal q-dot boundary. This juxtaposition depends on particle effective masses and band curvatures.) SPP excitations require sufficient local charge density that the plasma frequency ($\omega_p = \text{SQRT}\{Ne^2/\epsilon_0 m\}$) exceeds that of the optical field. This density corresponds approximately to degenerate doping levels. (With delta doping techniques the usually concomitant scattering from ion centers can be obviated.) Conversely, this carrier density can be provided by a single charge in a confined wavefunction, smaller than a few cubic nanometers.

If this suggested model pertains, it should have a distinct spectral signature. A descriptive wavefunction would likely propagate equatorially, and the concomitant resonance would reflect integer circumferential periods. The linewidth of such a spectral feature would depend on various aspects. First is the exciton recombination lifetime, itself dependent on interband wavefunction symmetry. Second is the surface plasmon polariton (SPP) scattering lifetime. The SPP lifetime has two components. SPP are inherently lossy, notably on planar surfaces. The electron polarization supported by the metal – or, alternatively, quasi free electron gas – exhibits Coulomb scattering aspects that introduce a loss tangent at optical frequencies. This is evident in the bulk spectral permittivity of e.g. noble metals. Lower loss tangent corresponds to a more nearly imaginary refractive index in the metal, a longer decay length for the transverse field distribution, and a less tightly bound propagating mode. (An alternative point of view incorporates Snell’s Law – equivalently, Maxwell’s equations – to convey that an exponential transverse field profile in the metal corresponds to a radiating field in vacuum that can be coupled to evanescently; and radiation indicates loss. This analysis is just a matter of matching real and imaginary parts of the propagation constant across a material boundary while noting that propagation in metals introduces an imaginary component.) Noting that some geometries, notably square cross-section metal strips, carry SPP-like modes with suppressed losses, in general metal-component waveguide structures intrinsically convey absorptive loss – that is, heat dissipative loss – to the propagating optical frequency field in addition to, and probably dominantly with regard to, incurred radiation loss. Second to consider is loss contributed by poor modal confinement. (Of course, we have just observed that evanescent propagating fields necessarily radiate – but here we examine geometric modal factors.) SPP are nominally transverse magnetic field excitations; but on a curved surface no field can be everywhere TM. (This statement excepts special singular geometries: the cylinder – or circular cross-section waveguide – supports circularly polarized modes as basis functions.) The question arises whether

bound modes exist on a sphere; the answer is no. From a different (i.e. external) perspective, this problem devolves into Mie scattering from small spherical particles. As a coupling problem, external Mie scattering cannot feasibly excite bound modes, only leaky modes. That said, bound modes might still exist, and might be stimulated by emission internal to the sphere surface. Mie-like analysis shows this impossible. A different approach to this conundrum advances by consideration of electromagnetic field behavior in a plasma, a metal being very similar in nature to a plasma. A mode represents a static field configuration; so $dE/dt = 0$. Under that constraint Maxwell's equations devolve to the force-free magnetic field condition represented by the curl eigenvalue equation: $\nabla \times B = \alpha B$. Solutions to this equation (see Marsh on Force Free Magnetic Fields) are nested toroidal magnetic surfaces, a magnetic surface being one on which the magnetic field is constant in magnitude. Continuing this exploration leads quickly to various aspects of topology, including multiply-connected manifolds, branch cuts in analytic complex valued functions, the physical import of electromagnetic gauge, and geometric (aka Berry) phase. Actually dynamically accessing such a static field configuration must proceed either asymptotically or by means of a dynamic phase transition prospectively invoking soliton structures. These explorations are beyond the scope of the present program. Returning to the issue of bound modes on a sphere, to the degree that any electromagnetic modes exhibit leaky energy behavior the apparent linewidth of the mode will broaden, adding to the other effects outlined previously. Penultimately this is good; an infinitesimal line cannot be excited. More likely, the linewidth would prove experimentally to be broader than optimal for a spectroscopic signal processing application (such as memory) unless a means to gate its response were discovered.

Considerations for Future Exploration

One of the underlying premises that originally promoted this work – that silicon nanospheres of discrete sizes could be easily and repeatedly produced electrochemically – has proved difficult to demonstrate. Other labs, notably those directed by M. Nayfeh, seem to have overcome these difficulties; so perhaps prospects endure. Were this demonstrable, mechanisms to convey silicon nanospheres to specific device sites might be developed. For example, silicon nanospheres might energetically aggregate at vicinal monolayer surface discontinuities (along dihedrals). Adopting a dramatically different approach, these nanospheres might be captured in an optical lattice to form an artificial crystal with properties determined by optical wavelength and intensity (via trapping potential depth) and interference periodicity (dependent on intersection angles). Work recently performed in D. Wineland's group at NIST demonstrates confinement of ions in mesoscopic Paul traps configured in silicon; optical interference in the same region might easily be introduced.

Alternative nanoscopic structures in silicon might exhibit preferred characteristics. (Whether they would self-delineate as these nanospheres seemingly do remains an open issue.)

For example, etching schemes might fabricate silicon nanorings (or nano-toroids) centered and stacked on silicon oxide pillars, with ring-to-ring separation established by atomic layer epitaxy techniques. Presuming carrier accumulation regions at the surface of these structures, SPP-like modes might be stimulated that exhibit both spectroscopic and nonlinear switching properties. Nanorings, vs. nanospheres, presumably exhibit bound modes that might be exploited to advantage. Silicon has also recently been found to show a near-infrared resonance in magnetic susceptibility that would couple to circulating charge conveyed in nanorings.

This speculation depends intimately on continued advances in techniques to nano-configure silicon. This is a daunting challenge that electrochemical methods were conceived to overcome. Producing reliable devices based on such structures assumes, as with modern MOSFET characteristics, emergence of schemes to suppress undesired carrier tunneling – as well as controlled electromagnetic (i.e. optical) confinement.

These points accepted, oscillations of electromagnetic fields at optical frequencies remain pertinent to nanoscopic structure interactions. Particularly in the near field (closer to an effective dipole than a wavelength, where retardation effects are negligible), electromagnetic fields – especially their magnetic components – exhibit distinctly different behavior.

Additionally, properties of charge behavior in two dimensional electron gas systems differ from those traditionally exploited. For example, in the presence of strong bias magnetic field the quantum (and fractional quantum) Hall effect appears, based on the circulation of electrons in quantized Landau levels. Quasi-particle (anyon) behavior is observed. Generally unappreciated, the magnetic field of a single spin at typical inter-electronic distances exceeds tens of Tesla, the scale of magnetic field required to invoke quantum Hall behavior.

Summary.

Present approaches are not compelling for device development.

Nanoscale functionality, however, remains incompletely explored. Optical frequency electromagnetic fields will almost certainly play a role at this scale, despite its being substantially sub-wavelength. Almost certainly two or three generations of technology will appear to populate the gap in dimension between current MOSFET gate linewidths (~20 nm) and molecular or atomic capabilities. Silicon is remarkably amenable to nanostructure techniques, and at quantized sizes interacts readily with optical fields despite its indirect bandgap in bulk samples.

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